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Abstract

Hard, adherent, 2-μm-thick lubricious silicon containing diamond-like carbon coatings (Si-DLC) were synthesized by 40 keV Ar^+ ion beam-assisted deposition (IBAD) of tetraphenyl-tetramethyl-trisiloxane oil on two, 5-cm × 5-cm × 0.64-cm-thick 4340 steel substrates. Two different substrate surface finishes were examined, one polished and one 600-grit finish (unpolished). The corrosion resistance of the Si-DLC coating was evaluated by electrochemical impedance spectroscopy (EIS) in a 0.005N concentration sodium chloride (NaCl) solution. Low-frequency impedance data from each of the coatings were compared with those of bare steel. The Si-DLC coating deposited on the polished substrate performed slightly better than the one deposited on the unpolished surface. Overall, the Si-DLC coating did not appear to offer very much corrosion protection to the steel. This was mainly attributed to the presence of defects in the coating. Furthermore, to study the effect of radiation on the electronic structure of the Si-DLC coating, three Si-DLC coatings synthesized under the same deposition conditions on silicon substrates at various oil precursor temperatures were irradiated by a 335-nm wavelength, 0.37 W, pulsed YAG laser at 35 kHz. Corrosion and irradiation results and procedures to minimize the pinhole density in the Si-DLC coating are discussed in detail.

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1. Introduction

Films of many promising tribological materials, including conventional diamond-like carbon (DLC), have been successfully deposited by ion beam-assisted deposition (IBAD). The friction coefficient of unlubricated DLC films in dry gases can be as low as 0.01, but this value can reach values as high as 0.10 and 0.20 when measured in a 10% relative humidity [1–3]. Various researchers [2–4] have shown that conventional DLC films doped with elements such as Si and Ti exhibit low pin-on-disk friction coefficients in humid environments. Amorphous DLC coatings have shown extremely smooth and dense surface morphology. These surface characteristics of the DLC coatings are highly desirable for corrosion protection applications. DLC films containing Si (Si-DLC) exhibit friction coefficients as low as 0.04 [2–4] at ambient humidity and temperature and are therefore highly promising for tribological applications. It has been also shown repeatedly that the adhesion of the Si-DLC coating on various substrates, including steel, has been excellent [4].

Electrochemical impedance spectroscopy (EIS) is a useful tool for determining the integrity of coatings. The electrochemical impedance of a "defect free" organic coating will initially act as a capacitor. However, latent discontinuities and imperfections will eventually cause ionically conducting, low, resistive paths perpendicular to the coated surface. The resistance of these pathways will decrease with exposure time [5]. During this time, low-resistance pathways tangential to the surface may form, followed by the initial under film corrosion [6]. DLC coatings have demonstrated promising barrier properties, such as remarkable resistance to nitric and hydrofluoric acid solutions, even after 2 hr of immersion [7].

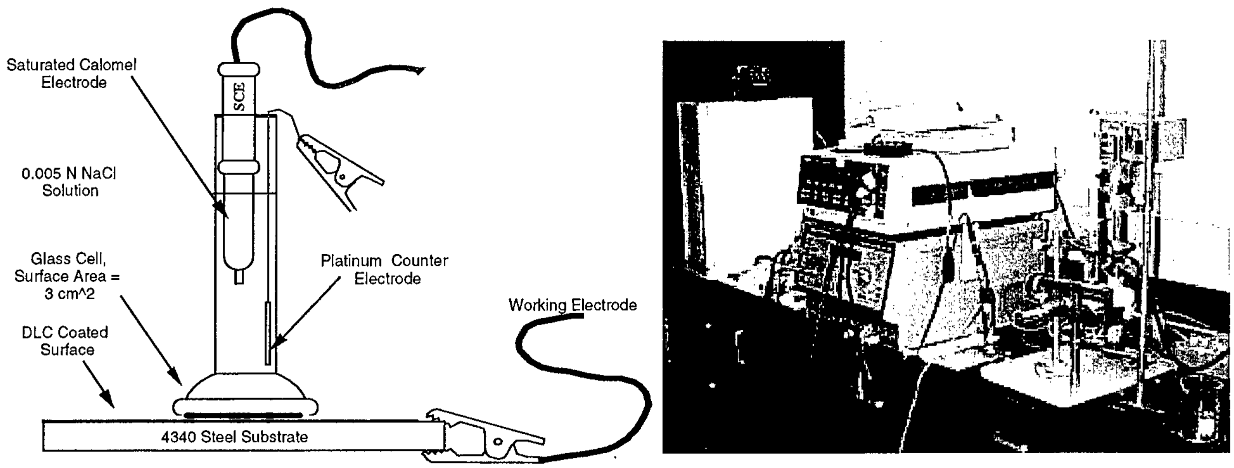
This report gives on the preliminary results of corrosion experiments on Si-DLC coatings synthesized on 4340 steel substrates by IBAD and the effect of the laser irradiation on the electronic structure of the Si-DLC synthesized on Si substrates.

2. Experimental Procedure

A ZYMET 100 nonmass analyzed ion implanter was used for synthesizing Si-DLC coatings using energetic Ar^+ ion bombardment of a vapor deposited tetraphenyl-tetramethyl-trisiloxane (Dow-Corning 704) diffusion pump oil with a precursor temperature of 140 °C. The Si-DLC was synthesized on 4340 substrates of two different surface finishes: polished (0.05–0.03-µm surface roughness) and unpolished 600 grit (0.4–0.2-µm surface roughness). Details on the synthesis of the Si-DLC coating using the ZYMET accelerator have been previously reported [4].

Three Si-DLC coatings synthesized on Si substrates at oil evaporation temperatures of 125 °C, 140 °C, and 155 °C were irradiated by a YAG Laser, 355-nm wavelength pulsed laser, 0.37 W, at 35 kHz. The thicknesses of the films were measured with the aid of a profilometer. The coating stoichiometry was determined by Rutherford Backscattering Spectrometry (RBS), and spectra were interpreted with the aid of the RBS simulation program RUMP [8].

Prior to the EIS, each sample was simply rinsed with distilled water and warm-air-dried. The EIS measurements were performed using a PAR Model 283 potentiostat/galvanostat, a Schumberger 1255 frequency response analyzer (FRA), and a personal computer (PC) using data acquisition software (Figure 1[b]). The software (Zplot) was used to compile the data, while data analysis and manipulation were done using Zview (Scribner Associates). A "batch" file was set up within Zplot to automatically take periodic measurements at set exposure times of 2, 6, 14, 30, 54, 78, and 102 hr. The cell used for the EIS experiments is shown in Figure 1(a). All EIS experiments were conducted using a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The surface area of the sample (working electrode) exposed for each measurement was 3.0 cm^2. Measurements were performed in a 0.005N NaCl solution at room temperature at open-circuit potential (OCP) over a frequency range of 100 kHz–0.01 Hz with an excitation amplitude of 30 mV. In preliminary testing of Si-DLC, the 0.5N NaCl solution was considered too severe for the coatings in this experiment, and so the solution was diluted to 0.005N NaCl.



(a) (b)

Figure 1. Schematic of the (a) Corrosion Cell and (b) Potentiostat and FRA Used in Experiment.

The collected data were plotted and analyzed in Bode format. The impedance of each sample, as defined by the log |Z| value at 0.01 Hz on the Bode plot, was then plotted vs. exposure time to show relative effectiveness of each sample over time. The OCPs were also recorded and plotted as a function of time.

3. Results and Discussion

3.1 Compositional Analysis, Friction, and Coating Morphology. Using the simulation program RUMP [8], the Si-DLC composition was determined to be $C_{67}Si_9O_6Ar_3H_{15}$. The average ball-on-disk coefficient of the Si-DLC was 0.08, and the average modulus of elasticity was 100 GPa.

Figure 2 illustrates the difference between the morphology of the two coatings. The coating on the polished substrate has far less and significantly smaller imperfections than the coating on the unpolished surface.

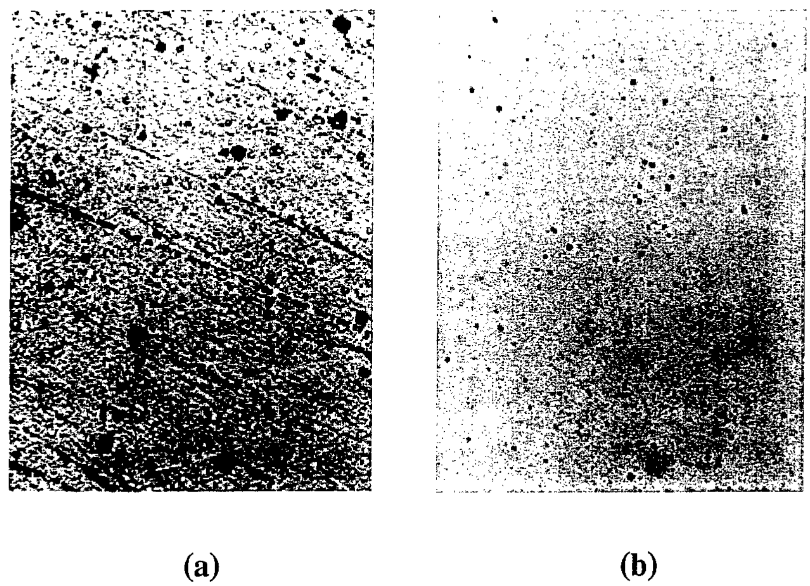


Figure 2. Photomicrographs (200×) of Si-DLC Coating on (a) Rough and on (b) Polished Substrate.

3.2 EIS Analysis Results. The EIS results of the Si-DLC coating on two surfaces finishes of 4340 steel are given in Figures 3 and 4. The total magnitude of the impedance |Z| at 0.01 Hz is plotted as a function of exposure time in 0.005N NaCl solution. Impedance values at low frequencies can distinguish between good and poor coatings [6].

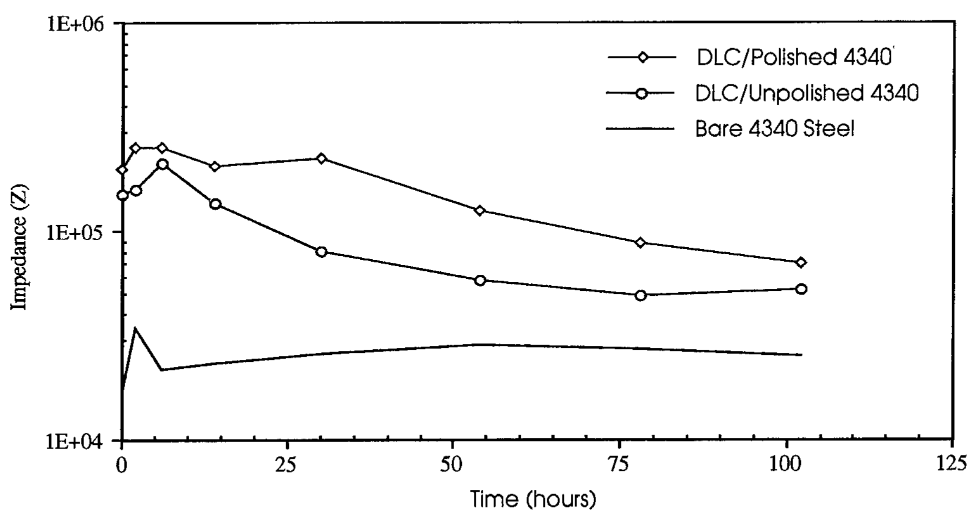


Figure 3. Low-Frequency Impedance of Bare and Si-DLC-Coated 4340 Steel as a Function of Time.

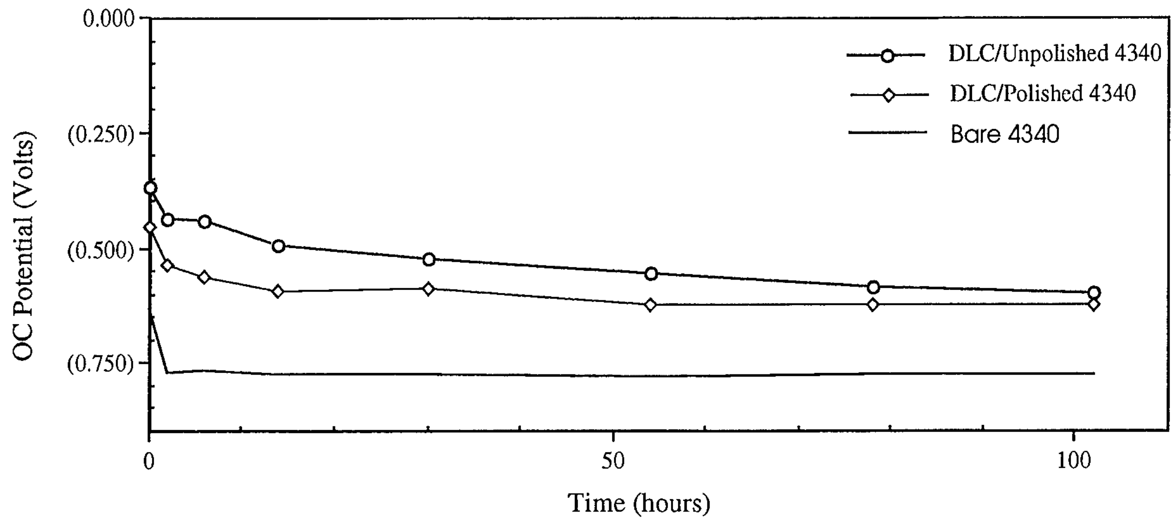


Figure 4. OCPs of Bare and Si-DLC-Coated 4340 Steel as a Function of Time.

Typically, sustained values of impedance in excess of 10^6 Ω/cm^2 indicate a stable protective barrier coating. As seen in Figure 3, even the highest values of the coatings failed to exceed that criteria. In fact, all impedance measurements were well under 10^6 Ω/cm^2, with the highest being slightly over 10^5 Ω/cm^2. The Si-DLC coating applied to the polished steel surface exhibited slightly better barrier properties than the coating on the rougher, unpolished substrate. Although the impedance of the Si-DLC samples was consistently higher than bare-steel sample, neither demonstrated acceptable barrier properties. Too many defects were present to make either of the coatings an effective barrier coating.

The higher OCP values of the coatings vs. the steel validates that the Si-DLC coatings are not providing sacrificial protection. For a coating to protect the steel in this capacity, the coating must have a lower corrosion potential OCP to allow it to be consumed before the steel. Figure 4 shows that both Si-DLC-coated samples are slightly more positive than the bare-steel sample.

The higher OCP of the Si-DLC on the unpolished substrate was quite unexpected. Typically, a barrier coating with larger defects is expected to have an OCP closer to that of the substrate (in this case, steel) than a coating with lesser defects. But the photomicrographs in Figure 2 show more and larger "imperfections" in the unpolished sample than in the coating on the polished substrate. Since the unpolished sample had many more and larger imperfections in the coating, it was expected to have a somewhat lower potential than the coating with far less imperfections. This was not the case. One possible explanation for the higher OCP in the unpolished sample is that the imperfections are localized high concentrations of carbon. X-ray photoelectron spectroscopy (XPS) analysis confirmed that the black spherical spots of Figure 2(a) do actually consist mainly of carbon. That, combined with the "pinhole" defects characteristic of these types of coatings, would create localized galvanic couples throughout the coating. The mixed potential of the two materials (i.e., steel and graphite) would be higher than the steel alone. Graphite has an OCP of about 0.2 V, while steel is about -0.7 V [9]. The sample with the greatest amount of these high carbon concentration "nodules" (the unpolished sample) should thus have a higher OCP.

The corrosion initiated at the pinhole defects in the Si-DLC coatings. Figure 5 is an illustration of the range of corrosion observed at varying distances from the point of maximum corrosion damage on the sample.

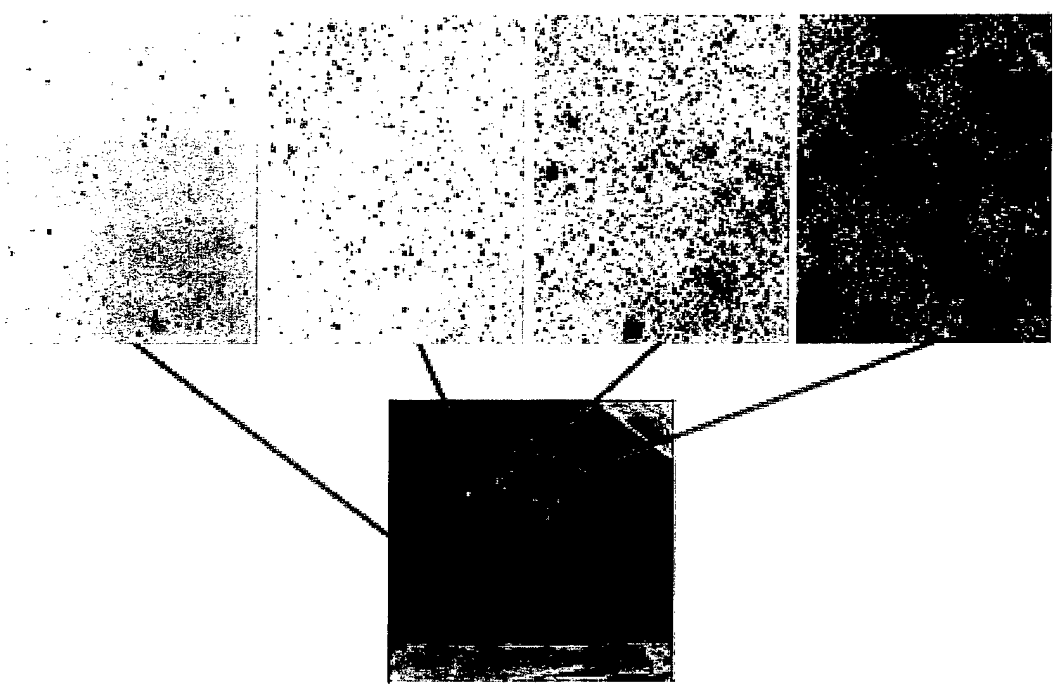


Figure 5. Illustration of the Nonuniform Corrosion of the Si-DLC Coatings (200×).

3.3 Laser Irradiation. Before laser irradiation, the valence band of the coating synthesized at 140 °C and 155 °C oil evaporation temperature was the same, but different than the valence band of the film synthesized at 125 °C. However, after the laser irradiation, the valence band for all coatings was the same (Figure 6). This may be attributed to the shift of some of the sp (2) domains due to the laser irradiation. Tabbal et al. [10] have also reported that an increase in laser intensity establishes some long-range order of the sp (2) domains in the deposited domains.

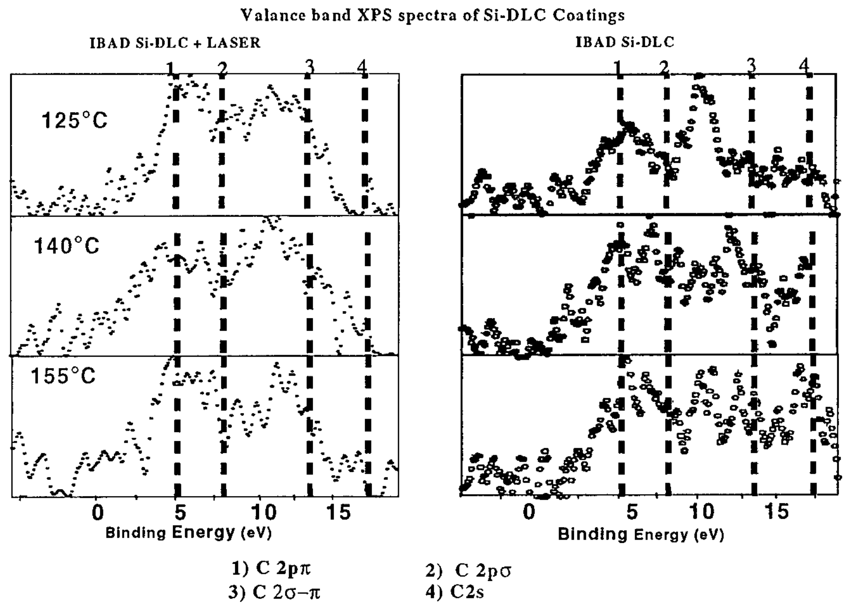


Figure 6. Effect of Laser Irradiation on the Electronic Structure of Si-DLC.

4. Conclusions

This work has demonstrated that the quality of the coating highly depends on the surface finish. The Si-DLC coating provided limited corrosion protection to steel in a 0.005 N chloride environment due to the existing pinholes in the coatings. Therefore, the coating defects need to be eliminated or blocked to improve the corrosion performance of these Si-DLC coatings. The laser irradiation resulted in coatings with the same valence band.

5. Future Work

To improve the corrosion resistance of the Si-DLC coating, the authors propose work in the following areas.

(1) Correlate the defect density (pinhole) with its degradation rate in a various hostile environments.

(2) Modify the deposition geometry to block the pinholes from "seeing" the steel substrate.

(3) Incorporate various metallic additives.

(4) Examine the possibility of a proper coating interlayer.

Finally, the influence of the laser irradiation on the valence band of the Si-DLC will be studied further.

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